

## PATENT SPECIFICATION

NO DRAWINGS

Inventor: VICTOR CHARLES ERNEST BURNOP



570,991

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## COMPLETE SPECIFICATION

## Metal-Organic Salt-Amine Complexes and their use in Hydrocarbon Oil Compositions

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to hydrocarbon oil-soluble complexes of certain metal salts and certain amines, and particularly to hydrocarbon solutions which contain such complexes.

Hydrocarbon oil solutions of metal salts may be used for a variety of purposes. For example solutions of copper salts may be useful for promoting the hardening of drying oil compositions. Many oil soluble salts find wide applications as lubricating oil additives.

In most instances the choice of metal salts which can be used in oil compositions is limited to those compounds which are oil soluble. In many cases the sole function of the action is to confer oil solubility on the metal ions. As a general rule it is found that metal salts of naphthenic acids are oil soluble whereas metal salts of fatty acids are sparingly soluble in oil. The Applicants have discovered, and this discovery forms the basis of the present invention, that oil-insoluble or sparingly soluble metal salts of fatty acids, chlorinated fatty acids and salicylic acid could be made oil soluble or have their oil solubility increased by forming a complex of the metal salt with certain aliphatic amines.

The present invention consists in a process for preparing hydrocarbon oil-soluble complex metal salts of a fatty acid, a chlorinated fatty acid or salicylic acid which comprises forming

a complex of a metal salt of the said organic acid with a branched-chain aliphatic primary amine by a) mixing the metal salt of the said organic acid with the amine at room temperature or at a temperature below the boiling point of the amine or below 200°C., whichever temperature is the lower or b) neutralizing the amine with the said organic acid, and then dissolving an oxide or base of the metal in the salt so formed.

The amines which may be used to make the complexes of the present invention may be secondary or tertiary alkyl primary amines. Such amines can be prepared from tertiary olefins, e.g. the various polymers of propylene and isobutene; copolymers of propylene and isobutene; and copolymers of isobutene and butenes or pentenes. Such polymers and copolymers are well known synthetic olefins in the petroleum industry. However, in such polymerizations, various isomerizations and migrations may occur such that a mixture of olefins is produced. Thus, a tertiary alkyl primary amine prepared from tri-isobutene may contain tertiary alkyl primary amines of 13, 14 and/or 15 carbon atoms as well as the predominant one of 12 carbon atoms. Similarly, when making a tertiary alkyl primary amine of 18 carbon atoms from hexamethylene, a polymer of propylene, one may obtain a mixture of tertiary alkyl primary amines having predominantly 18 carbon atoms per molecule with minor amounts of homologous molecules with 19, 20, 21, 22, 23 and/or 24 carbon atoms. Such a mixture is conveniently designated "T-C<sub>18-24</sub> H<sub>1-24</sub> NH<sub>2</sub>".

Specific examples of amines or mixtures thereof which may be used include the following:

- 3 - amino - 3,5,8 - trimethyl - nonane  
 5 - amino - 5,13 - dimethyl - hendecane  
 3 - amino - 3,5,7,9,12 - pentamethyl - tri-  
 decane  
 5 4 - amino - 2,4,6,8,10 - pentaamethyl - tri-  
 decane  
 2 - amino - 2,4,4,6,6,8,8 - heptaamethyl-  
 nonane  
 10 6 - amino - 2,2,4,4,6,8,8 - heptaamethyl-  
 nonane

Further we have discovered that the amines which are most suitable for forming these complexes are branched chain amines containing from 8 carbon atoms and less than 30 carbon atoms. Particularly preferred amines are the mixture of amines obtained by reacting tetrapropylene with ammonia. It will be noted that these amines contain a highly branched structure, and consist of  $C_{12}$  amines. Other amines for use in the present invention are obtained by reacting ammonia with polymerized olefins containing 18 to 24 carbon atoms, these olefins having been obtained by known processes for polymerizing and copolymerizing simple olefins such as propylene and isobutylene.

The fatty acids and chlorinated fatty acids used in the formation of the complex may be  $C_2$  to  $C_{22}$  fatty acids, or chlorinated fatty acids, e.g. acetic and monochloroacetic acid. Mono or dichlorinated fatty acids containing from 2 to 6 or 2 to 4 carbon atoms are preferred. Suitable metals that may be used in the complex are cadmium, cobalt, copper, silver and zinc.

By means of the present invention it is possible to obtain hydrocarbon solutions of metal salts by converting hydrocarbon oil insoluble or sparingly soluble salts into oil soluble complexes. As hereinafter described a variety of compounds may be conferred with the property of oil solubility. Further it will be realized that by means of the present invention it is possible to convert cheap and readily available oil insoluble substances into an oil solution.

When using method a) for the preparation of the complexes of this invention from 1 to 8 mols of the amine may be used for each mol of the salt. We have found that a preferred complex may be derived from about 2 mols of amine to 1 mol of salt. It is therefore preferred to use about 1.5 mols to 3 mols of amine per mol of salt. The amine solution of the complex may be diluted with hydrocarbon oil and the solution filtered if necessary.

Method b) as hereinbefore described is of particular application where the metal salt of the organic acid is deliquescent (see Examples 2 and 3).

To facilitate the explanation of the process of preparing the complex of this invention some specific examples will be included.

#### EXAMPLE 1

Copper stearate is sparingly soluble in white oil. The Applicants discovered that if solid anhydrous copper stearate is stirred at room temperature with Primene J.M.T. (described below) the copper stearate dissolves in the amine. Copper and cobalt salts tend to form the deep blue colour associated with amine complexes. When the copper stearate was dissolved in the amine, the solution was then diluted with white oil and a solution of the complex in oil was formed. In the example of copper stearate the excess amine was removed by evaporation and the complex remaining contained 1.7 mols of amine to 1 mol of stearate.

#### EXAMPLE 2

343 gm. of Primene J.M.T.<sup>a</sup> were neutralized by the addition of 60 gm. of acetic acid and 40 gm. of zinc oxide were stirred in and dissolved at 120-150°C with nitrogen blowing to remove the water formed. The product was a viscous liquid which was oil soluble.

<sup>a</sup>Primene J.M.T. is a mixture of  $C_{10}$ - $C_{12}$ , alkyl branched chain primary amines.

Primene 81-R is a mixture of  $C_{11}$  alkyl branched chain primary amines.

"Primene" is a Registered Trade Mark.

#### EXAMPLE 3

In a similar preparation 945 gm. of chloroacetic acid were used instead of the acetic acid in Example 1 to give on cooling a brown resin which was oil soluble.

#### EXAMPLE 4

63 gm. of zinc stearate were dissolved by warming to 80°C with 38 gm. of Primene 81-R to give a viscous product which was oil soluble.

There are included in Table 1 the results of a series of tests to test the property of various metal salts of organic acids to form complexes with Primene 81-R. The metal salt was warmed with 2 molecular proportions of the amine. The following salts dissolved readily and were not precipitated by dilution with white oil.

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TABLE I

Cobalt stearate	Zinc octoate
Copper octoate	Zinc octoate
Copper octoate	Zinc caprate
Copper stearate	Zinc propionate
Copper propionate	Zinc stearate
Silver stearate	Zinc salicylate
	Cadmium stearate

5 Zinc chloracetate formed a soluble complex when at least 4 mols of aliphatic amine were used. Again this complex was not precipitated on dilution with white oil.

The complexes prepared from 1 mol zinc diethyldithiocarbamate and 2 mols. Primenes J.M.T. or 81-R are also oil-soluble.

In most cases the complexes are completely miscible with oil. However, the solubility of the different complexes varies and Table II shows the solubility at room temperature of zinc stearate in a variety of amines.

TABLE II

Solubility of Zinc Stearate in Five Molecular Proportions of Amine

Soluble at room temperature	Wt. amine/stearate
Aliphatic amine <sup>a</sup>	1.5
Soluble at 60° C.	
2-ethylhexylamine	1.0
2-dimethyl(amino)ethanol	0.7
Soluble at 100° C.	
di-(2-ethylhexyl)amine	1.9

<sup>a</sup> Aliphatic amine is a mixture of C<sub>10</sub> amines obtained by reacting with propylene with ammonia.

20 By means of our invention it is possible to obtain a wide range of oil soluble complexes of metal salts of the acids heretofore described. These hydrocarbon oil solutions may be put to a variety of uses. By suitable choice of the constituents of the oil soluble complex, for example, certain of the complexes containing copper may be used as fungicides, or as additives for diesel fuels, e.g. to decrease exhaust smoking.

25 Certain silver based complexes may be used as preignition inhibitors. Certain complexes may be used as lubricant additives; zinc based complexes are preferred and the

Applicants have further discovered that, if the acid constituent of the complex contains chlorine or sulphur substituents, then certain of these additives are especially suitable as additives for anti-wear or extreme pressure lubricants.

The amount of additive used in the lubricating oils, fuels or fungicides may be 0.01 to 20% by weight, based on the total composition. About 1% of the additive is the generally preferred amount.

The additive is also soluble in various non-hydrocarbon oils. Thus the lubricating oils in which the additive may be used include

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both natural and synthetic oils, e.g. ester oils and polyorganosilylene ether and ester oils.

It is important for the reduction of valve burning to lower the phosphorus content of crankcase lubricants, which in effect means decreasing the concentration of any phosphorus compound added to the oil. It has been found that mixtures of the amine complexes with dithiophosphates have better P.P. properties than the individual components. Thus a preferred embodiment of the invention comprises a lubricating oil containing an oil-soluble complex of a metal salt of an organic acid and an aliphatic amine as hereinbefore defined, and a dialkyl dithiophosphate.

The preferred dithiophosphates are zinc dialkylidithiophosphates. The alkyl groups of the dithiophosphates are preferably derived either from 70/30 parts by weight mixture of methyl isobutyl carbinol and isopropanol (Additive A), or from 65/35 parts by weight mixture of primary  $C_{10}$  and primary  $C_{12}$  Oxo alcohols (Additive B).

The amount of dithiophosphate used may be up to 10% by weight, e.g. 0.1% to 2%, and is preferably about 1%.

In addition to the above dithiophosphates, other lubricating additives, e.g. a mixture of calcium or barium petroleum sulphonate and  $P_2S_5$ , treated polybutene, or a mixture of barium phenate and  $P_2S_5$ , treated polybutene, may be added to the lubricating oil compositions.

Lubricating compositions containing the complexes of this invention with or without the addition of dithiophosphates, were tested to evaluate their properties in the following way:—

#### Four Roll Machine Results

The antiwear properties of lubricants may be assessed by running in the Four Roll Machine for a given time at a fixed load, and results for a number of oils containing Zinc salt complexes are given in Table 3. A smaller scar corresponds to improved antiwear properties.

Alternatively, the scar diameter may be determined at a fixed interval at different loads. The scar diameter increases slightly as the load increases, until at a load corresponding to the change from "sliding" to "tearing" scar diameter becomes much larger.

This load, referred to as the critical load, is a measure of the Extreme Pressure Properties of the lubricant. Finally the weld load, corresponding to welding in one minute, measures the ability of the lubricant to prevent seizure.

#### EXAMPLE 5

In table III two zinc salt complexes in an SAE 30 mineral lubricating oil are compared with the base oil, and it is seen that the complexes improve the load carrying ability of the oil.

In table IV, it is seen that mixtures of Zinc acetate or Zinc chloroacetate complexes with ZDDP have better P.P. properties than the components taken singly.

#### Engine Test (Corrosion Inhibition Test)

In the Standard Chevrolet L4 Test procedure, the bearing weight (copper-lead bearing) loss for a 2% blend of Zinc-octanoate Phosphate J.M.T. complex in a SAE 30 base mineral oil was 225 mg. For the base oil alone the loss was 1160 mg.

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TABLE III  
Four Ball Machine Wear Score at One Minute  
(Millimeters)

Load in Kg	20	40	50	55	60	70	75	80	90	95	Critical load	Weld load
SAE 30 Box Oil	.26	.34	.40	1.80	1.96						53 Kg	180 Kg
1.3% Zinc Acetate — Primene J.M.T. complex <sup>a</sup>	.26	.34	.36	—	.38	.50	2.12	2.20			70 Kg	160 Kg
1.5% Zinc Chloracetate — Primene J.M.T. complex <sup>a</sup>	.28	.35	.38	—	.42	.44	—	.46	.53	1.90	92 Kg	240 Kg

<sup>a</sup> corresponds to 0.1% Zinc by weight in oil blend concentrations by weight.

TABLE IV  
Four Ball Machine Results

Lubricant	Obtained Load (Kg)	Weld Load (Kg)
0.65% Zinc Acetate -- Primene J.M.T. complex	62	152
1.30% " " " "	70	160
0.75% Zinc Chloroacetate -- Primene J.M.T. complex	94	249
1.50% " " " "	92	240
0.60% Additive A (1)	94	249
0.60% Additive B (2)	98	203
1.20% Additive A	90	240
1.20% Additive B	90	216
0.60% Additive A + 0.65 Zinc Acetate complex	114	240
0.60% Additive B + 0.65 " " "	122	192
0.60% Additive A + 0.75 Zinc Chloroacetate complex	114	390
SAR 30 Base Oil	53	160

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## EXAMPLE 6

The compositions shown in Table V were tested by the four Ball Machine Test. The complexes were obtained by dissolving one

gm. mole of the zinc salt in 2 gm. moles of Primene 81-R, at room temperature. The complex so obtained was dissolved in the oil.

TABLE V

Shell Four Ball Machine Test

Lubricant	Wear scar diameter (mm) or 15 Kg load/hour/1450 r.p.m.	Weld load Kg
Base SAE 30 mineral lubricating oil	0.50	150
0.72 vol. % Primene 81-R	0.60	—
Zinc acetate — Primene 81-R complex	0.30	150
Zinc propionate " " "	0.35	—
Zinc caprylate " " "	0.33	—
Zinc salicylate " " "	0.30	—
Zinc chloroacetate " " "	0.13	240

Note: The concentration of all zinc compounds in the above table is such that the zinc concentration is 0.1% in each case, and the Primene 81-R concentration of 0.72% is sufficient to give the complex  $ZnA_2 \cdot 2RNH_2$  (where A is the acid radical of the organic acid) at this zinc concentration.

## WHAT WE CLAIM IS:—

- 10 1) A process for preparing hydrocarbon oil-soluble complex metal salts of a fatty acid, chlorinated fatty acid or silicylic acid, which comprises forming a complex of a
- 15 metal salt of the said organic acid with a branched chain aliphatic primary amine, by a) mixing the metal salt of the said organic acid with the amine at room temperature or at a temperature below the boiling point of the amine or below 200°C., whichever tem-
- 20 perature is the lower, or b) neutralizing the amine with the said organic acid, and then dissolving an oxide or base of the metal in the salt so formed.
- 25 2) A process as claimed in claim 1 wherein the metal salt is a salt of cadmium, cobalt, copper, silver or zinc.
- 3) A process as claimed in claim 1 or 2 wherein the amine is a mixture of  $C_{12}$  alkyl branched chain primary amines or a mixture

of  $C_{12}$  to  $C_{18}$  alkyl branched chain primary amines.

4) A process for preparing the compound claimed in any of claims 1 to 3 which comprises mixing 1 to 8 molecules of the amine with 1 molecule of the salt.

5) An oil soluble complex wherever prepared by the processes of claims 1 to 4.

6) An oil soluble complex as claimed in claim 5 which is a complex of zinc acetate and a mixture of  $C_{12}$  to  $C_{18}$  alkyl branched chain primary amines.

7) A composition comprising a hydrocarbon oil and the oil-soluble complex according to claim 5 or claim 6.

8) A composition as claimed in claim 7 containing also a zinc dialkyl dithiophosphate.

K. J. VERYARD,

50 SUMNER STREET, W.L.  
Agent for the Applicant.

## PROVISIONAL SPECIFICATION

## Metal-Organic Salt-Amine Complexes and their use in Hydrocarbon Oil Compositions

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do

hereby declare this invention to be described in the following statement:—

The present invention relates to oil-soluble complexes of a metal salt and an aliphatic amine and particularly to hydrocarbon solu-

ness which occurs in these complexes.

Hydrocarbon oil solutions of certain inorganic metal compounds may be used for a variety of purposes. For example solutions of copper salts may be useful for promoting the hardening of drying oil compositions. Many oil soluble salts find wide application as lubricating oil additives. In general the metal compound is an electro-valent compound and the desired property conferred on the composition is due mainly to the metal ion of this compound.

In most instances the choice of metal electro-valent compounds which can be used in oil compositions is limited to those compounds which are oil soluble. In many cases the sole function of the anions is to confer oil solubility on the metal ions. As a general rule it is found that metal salts of naphthenic acids are oil soluble whereas metal salts of fatty acids are sparingly soluble in oil. The use of salts of fatty acids is therefore restricted to grease compositions.

The Applicant investigated methods for converting oil insoluble metal salts of organic acids, into oil soluble complexes. As a result of this investigation, the Applicant has discovered, and this discovery forms the basis of the present invention, that certain metal salts of organic acids could be made oil soluble or have their oil solubility increased by forming a complex of the metal salt with certain aliphatic amines.

The composition of the present invention therefore comprises a hydrocarbon oil solution of an oil soluble complex of the metal salt of an organic acid and an aliphatic amine.

By means of the present invention it is possible to obtain hydrocarbon solutions of metal salts by converting hydrocarbon oil insoluble salts into oil soluble complexes. As hereinafter described a variety of compounds may be conferred with the property of oil solubility. Further it will be realized that by means of the present invention it is possible to convert cheap and readily available oil insoluble substances into an oil solution. Obviously oil solutions of these oil soluble compositions will have many uses.

The composition of the present invention may be made in the following manner. The metal salt of the organic acid is mixed with the aliphatic amine at room temperature or at a temperature below the boiling point of the amine or below 200°C., whichever temperature is the lower. From 1 to 8 mols of the amine should be used for each mol of the salt. We have found that a preferred complex may be derived from about 2 mols of amine to 1 mol of salt. It is therefore preferred to use about 1.5 mols to 3 mols of amine per mol of salt. The amine solution of the complex may be diluted with hydrocarbon oil and the solution filtered if necessary.

An alternative method of preparing the complex comprises neutralizing the amine with the organic acid and then dissolving the salt or base of the metal in the oil so formed. The complex is then dissolved in the hydrocarbon oil. This method is of particular application where the metal salt of the organic acid is deliquescent (see Examples 2 and 3 below).

To facilitate the explanation of the process of preparing the complex of this invention some specific examples will be included.

#### EXAMPLE 1

Copper stearate is sparingly soluble in white oil. The Applicant discovered that if solid anhydrous copper stearate is stirred at room temperature with Primene J.M.T. (described below) the copper stearate dissolves in the amine. Copper and cobalt salts tend to form the deep blue colour associated with amine complexes. When the copper stearate was dissolved in the amine, the solution was then diluted with white oil and a solution of the complex in oil was formed. In the example of copper stearate the excess amine was removed by evaporation and the complex remaining contained 1.7 mols of amine to 1 mol of stearate.

#### EXAMPLE 2

343 gm of Primene J.M.T.<sup>o</sup> were neutralized by the addition of 60 gm of acetic acid and 40 gm of zinc oxide were stirred in and dissolved in 120°-150°C with nitrogen blowing to remove the water formed. The product was a viscous liquid which was oil soluble.

<sup>o</sup>Primene J.M.T. is a mixture of C<sub>10</sub>-C<sub>12</sub> branched chain primary amine. Primene 81-R is a mixture of C<sub>12</sub> branched chain primary amine.

#### EXAMPLE 3

In a similar preparation 945 gm of chloroacetic acid were used instead of the acetic acid in example 1 to give on cooling a brown resin which was oil soluble.

#### EXAMPLE 4

63 gm of zinc stearate are dissolved by warming to 80°C with 30 gm of Primene 81-R to give a viscous product which was oil soluble.

#### EXAMPLE 5

Zinc oxide dissolved in stirred and heated Primene J.M.T. (C<sub>10</sub>-C<sub>12</sub>) at 150°C, the water produced being blown out by a stream of nitrogen.

There are included in table 1 the results of a series of tests to test the property of various metal salts of organic acids to form complexes with Primene 81-R. The metal



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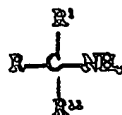
oil was washed with 2 molecular proportions of the aliphatic amine". The following salts dissolved readily and were not precipitated by dilution with white oil.

TABLE I

Complex forming	Zinc acetate
Cobalt acetate	Zinc acetate
Copper acetate	Zinc caprate
Copper sebacate	Zinc propionate
Copper stearate	Zinc stearate
Copper propionate	Zinc salicylate
Silver stearate	Cadmium acetate

Zinc chloroacetate formed a soluble complex when at least 4 mols of aliphatic amine were used. Again this complex was not precipitated on dilution with white oil.

- 10 The amine materials which may be used to make the complexes of the present invention include tertiary alkyl primary amines of the general formula:



- 15 wherein R, R<sup>1</sup> and R<sup>11</sup> are straight or branched chain alkyl radicals of 1 to 18 carbon atoms; the total number of carbon atoms in the molecule being 12 to 24. These amines can be prepared from tertiary olefins, e.g. the various polymers of propylene and isobutene; copolymers of propylene and isobutene; copolymers of isobutene and butenes or pentenes; etc. Such polymers and copolymers are well known synthetic olefins in the petroleum industry. However, in such polymerizations, various isomerizations and migrations may occur such that a mixture of olefins are produced. Thus, a tertiary alkyl primary amine prepared from tri-isobutene may contain tertiary alkyl primary amines of 13, 14 and/or 15 carbon atoms as well as the predominant one of 12 carbon atoms. Similarly, when making a tertiary alkyl primary amine of 18 carbon atoms from hexopropylene, a propylene, one may obtain a mixture of tertiary alkyl primary amines having predominantly 18 carbon atoms per molecule with minor amounts of homologous molecules with 19, 20, 21, 22, 23 and/or 24 carbon atoms. Such a mixture is conveniently designated



Specific examples of amines or mixtures thereof which may be used include the following:

- 3 - amino - 3,5,8 - trimethyl - paraffin  
5 - amino - 5,13 - dimethyl - heptadecane  
3 - amino - 3,5,7,9,12 - pentaethyl - tri-decane  
4 - amino - 2,4,6,8,10 - pentaethyl - tri-decane  
2 - amino - 2,4,6,8,10,12 - hexamethyl - nonane  
6 - amino - 2,2,4,4,6,8,8 - heptamethyl - nonane

Further we have discovered that the amines which are most suitable for forming these complexes are branched chain amines containing more than 8 carbon atoms and less than 30 carbon atoms. Particularly preferred amines are the mixture of amines obtained by reacting isopropylamine with ammonia. It will be noted that these amines contain a highly branched structure, and consist of C<sub>12</sub> amines. Other amines for use in the present invention are obtained by reacting ammonia with polymerized olefins containing 18 to 24 carbon atoms, these olefins having been obtained by known processes for polymerizing and copolymerizing simple olefins such as propylene and isobutylene. Secondary aliphatic amines may also be used and it is preferable that these secondary amines are part of the cyclic structure, such as morpholine, cyclohexylamine, and N alkyl derivatives thereof. Aliphatic secondary amines containing more than 4 carbon atoms may also be used, for example diethylamine.

Table 2 shows the solubility at room temperature of zinc acetate in a variety of amines. This table illustrates the scope of the present invention.

TABLE 2

## Solubility of Zinc Stearate in Five Molecular Proportions of Amine

Soluble at room temperature	Wt. amine/stearate
Aliphatic amine <sup>a</sup>	1.5
Soluble at 60° C.	
Triethylamine	1.2
Morpholine	0.7
Cyclohexylamine	0.8
2-ethylhexylamine	1.0
2-dimethylaminooctanol	0.7
diethanolamine	0.8
Soluble at 100° C.	
dioctylamine	0.8
tetraethylammonium pentamine	1.5
di-(2-ethylhexyl) amine	1.9
cetyl amine	1.9
propylene diamine	0.6
Insoluble at 100° C.	
tri-n-octylamine	2.8
ethylene diamine	0.5

<sup>a</sup> aliphatic amine is a mixture of C<sub>12</sub> amines obtained by reacting tri-n-propylene with ammonia.

The metals that may be used in the complex are cadmium, cobalt, copper, silver, zinc.

The preferred class of these acids are derived from the following fatty acids, chlorinated fatty acids, e.g. acetic, monochloroacetic acid, and allylic acid. Mono or dichlorinated fatty acids containing from 2 to 6 or 2 to 4 carbon atoms are preferred.

By means of our invention it is possible to obtain a wide range of oil soluble complexes of metal salts. These hydrocarbon oil solutions may be put to a variety of uses. By suitable choice of the constituents of the oil soluble complex, the complex of cerium of the complexes containing copper may be used as fungicides, or as additives for diesel fuels, e.g.

to decrease exhaust sooting. Certain silver based complexes may be used as pre-ignition inhibitors. Certain zinc based complexes may be used as lubricant additives. The Applicants have further discovered that if the acid constituent of the complex contains chlorine or sulphur substituents then certain of these additives may be used as additives for anti-wear or extreme pressure lubrication.

## EXAMPLE 6

The compositions shown in table III were tested by the Four Ball Machine Test. The complexes were obtained by dissolving one gm mole of the zinc salt in 2 gm moles of the Primene 81-8, at room temperature. The complex so obtained was dissolved in the oil.

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TABLE 3

## Shell Four Ball Machine Test

Lubricant	Wear scar diameter (mm) at 15 Kg load/1 hour/1450 r.p.m.	Weld load Kg
Base oil	0.50	150
0.72 vol. % Primene 81-R	0.60	—
Zinc acetate — Primene 81-R complex	0.30	150
Zinc propionate „ „ „	0.35	—
Zinc crotonate „ „ „	0.33	—
Zinc salicylate „ „ „	0.30	—
Zinc chloroacetate „ „ „	0.13	260

Note: The concentration of all zinc compounds in the above table is such that the zinc concentration is 0.1% in each case, and the Primene 81-R concentration of 0.72% is sufficient to give the complex  $ZnA_2ENH_2$  at this zinc concentration.

K. J. VERYARD,  
33, Davies Street,  
London, W.1,  
Agent for the Applicants.

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